# X-RAY DIFFRACTION EXAMINATION OF INTERCALATED ALKYLAMMONIUM HUMATE COMPLEXES

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By exchange of the cations of humate extracted from brown coal with an equivalent quantity of long-chain organic cations, the following organophilic humate samples were prepared: *n*-decyl, *n*-dodecyl, *n*-tetradecyl, *n*-hexadecyl and *n*-octadecyl-ammonium humate. X-ray diffraction examination of the humic acid and the alkylammonium humates revealed behaviour similar to that of smectite-type clay minerals. The results clearly support the theory of the layer structure of humic acid. Calculations on the basis of the Brindley model indicate that the humate layers are 4.65 Å thick and that the double layer of the alkylammonium cations bound to the carboxyl and phenolic hydroxyl groups in the interlayer space is oriented at 53.25° relative to the planes.

## *Introduction*

Humic substances are of natural origin. They are dark brown, hydrophilic, acidic, high molar mass, polydisperse substances. They contain acidic functional groups, such as carboxyl and phenolic hydroxyl, which dissociate to varying degrees depending on the pH of the solution and the concentration of the electrolyte. As concerns physical-chemical characteristics, they display features of both polyelectrolytes [1], and association colloids [2].

Several research workers [3] have examined the chemical structures of humic substances with different methods for a long time. No exact structure can be given, as a result of the chemical complexity of humic substances. Various conceptions have been put forward. BURGES ET AL. [4] consider that their structure is similar to that of other natural macromolecules and they are polycondensates of a random collection of phenolic units. HAWORTH [5] thinks that the basis of their structure is a complex aromatic nucleus, to which polysaccharides, proteins, simple phenols and metals are attached physically or chemically. According to SCHNITZER [3], fulvic acids (a group of humic substances) are built up from aromatic oxycarboxylic acids. These "building blocks" are attached to each other through hydrogen-bonds.

The steric structure of the particles of humic substances is questionable. Are they linear, flexible chains which, depending on the dissociation of the functional groups, roll up to various extents? Do they form a statistical coil? Or are they planar aromatic ring systems which can arrange themselves in certain circumstances?

From their examinations of humic acids by ultracentrifugation, FLAIG and BEUTELSPACHER [6] came to the conclusion that they are spherical colloids. On the

basis of small angle X-ray scattering, WERSHAW ET AL. [7] propose that larger particles of humic acid are elliptical, while smaller ones are spherical. Humic substances have been examined by means of viscosity measurements by several authors [3]. The substances uniformly showed polyelectrolyte characteristics. The polyanions of humic substances are linear chains and/or spherical colloids.

X-ray diffraction examination of solid humic substances of natural origin demonstrated that they are not crystalline [3]. In the X-ray diffraction pattern of a powder specimen of fulvic acid, KODAMA and SCHNITZER [8] found a diffuse band at 4.1 Å, accompanied by a few minor humps. These humps were similar to those given by carbon black, which contains graphite-like layers. With respect to the carbon skeleton of fulvic acid, they stated that it was a network of poorly condensed aromatic rings. From X-ray examinations KASATOCHKIN ET AL. [9] concluded that humic substances contain a flat condensed aromatic network, to which side-chains and functional groups are attached.

The X-ray examinations reported in the literature, which could indicate the steric structure, the globular or lamellar shape of the molecules of humic substances, or the planar structure of the condensed aromatic ring system, are not convincing. The result usually is that very uncharacteristic, diffuse diffraction patterns are formed, since the flakes, even if they existed in a dissolved state, are not satisfactorily arranged in the solid sample. PFIRRMANN and WEISS [10, 11] made an X-ray diffraction study of humates organophilized by long alkyl-chain cation-active compounds. They obtained sharp reflexions at angles depending on the length of the alkyl chain.

Though the crystal structure of montmorillonite is that of a layer silicate built up from two $SiO_4$ tetrahedral sheets and one $AlO_4$ octahedral sheet, the basal spacing ($d_{001}$) X-ray diffraction peak is diffuse [12]. Sharp peaks are found, however, if the cations in exchangeable positions are exchanged for long-chain organic cations, since as a result of the interaction between the alkyl chains the flakes lie in order on top of each other [13].

Our starting point was that by reacting the negatively charged functional groups of humates with long-chain organic cations, we should observe behaviour similar to that of montmorillonite organocomplexes if the humate particles were originally planar in structure.

## *Experimental*

The humic acid sample examined was extracted from Hungarian brown coal (Tatabánya) with 0.1 mol $dm^{-3}$ potassium hydroxide. Purification of the crude humic acid was carried out in the usual way, as described by SCHNITZER and KHAN [3]. The elementary composition of the humic acid was C: 54.01%, H: 4.32%, O: 34.86%, N: 3.08%, its ash-content was 3.72%, and its cation exchange capacity was 4.1 meq $g^{-1}$. By means of membrane osmometry and extrapolation as applied in the measurement of the molar mass of polyelectrolytes [14], the number-average molecular weight of the sample was found to be $\overline{M}_n = 10\,600$.

*Preparation of n-alkylammonium organocomplexes*

Humic acid was dissolved in an equivalent quantity of sodium hydroxide to give a 1 g/100 $cm^3$ sodium humate solution. The alkylammonium chlorides were made by dissolution of alkylamines in an equivalent quantity of HCl. With increase of the length of the alkyl chain, the alkylammonium become less soluble in water, so the solution were made at 60 °C. 0.1 mol $dm^{-3}$ *n*-decyl, *n*-dodecyl and *n*-tetradecylammonium chloride, 0.05 mol $dm^{-3}$ *n*-hexadecylammonium chloride and 0.03 mol $dm^{-3}$ *n*-octadecylammonium chloride solutions were made. The organocomplexes were also made at 60 °C, equivalent quantities of alkylammonium salts being added to sodium humate solution. The suspensions were kept at 60 °C for one day, then filtered and washed chloride-free with approx. 60 °C distilled water. The substances were dried under infrared light and then ground. The powder samples were examined by X-ray diffraction with a DRON-3 Soviet-made diffractometer.

*Results*

Diffractograms of humic acid and the various alkylammonium humates (2—12° angle range) can be seen in Fig. 1. The alkylammonium humates, especially with those with longer alkyl chains, give high-intensity sharp peaks, in contrast with the diffuse, uncharacteristic diffraction pattern of humic acid. With increase of the length of the alkyl chain, the reflexions shift towards lower $2\theta$ values and become sharper. The distances between the humate flakes were calculated from the reflexion values *via* the Bragg equation, supposing clay mineral analogy and regarding the peaks as $d_{001}$ distances:

$$d_{001} = \frac{\lambda}{2}\frac{1}{\sin\theta}$$

where $\frac{\lambda}{2}$=0.77092 (CuK$\alpha$).

The results are given in Table I.

When the distance between the humate flakes was plotted as a function of the length of the alkyl chain in the alkylammonium cations (see Fig. 2), a linear connection was found, similarly to those for the alkylammonium intercalation complexes of montmorillonite and vermiculite [13].

With regard to the analogous behaviour, the results were evaluated on the basis of the Brindley model [15] for the primary alkylammonium complexes of montmorillonite and vermiculite. The model considers the geometry (the orientation relative to the flakes) of the straight-chain alkylammonium cations in the space between the clay mineral layers from the distances ($d_{001}$) between the

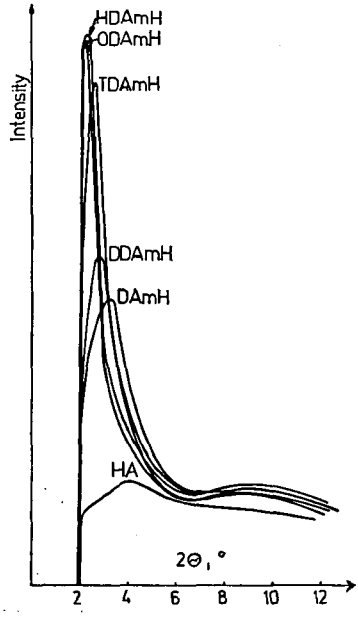


*Fig. 1.* X-ray diffraction patterns of primary alkylammonium humates and humic acid

*Table I*

| Sample | Quantity of alkyl-ammonium cations % | 2θ, ° | $d_{001}$, Å | | Relative intensity |
|---|---|---|---|---|---|
| | | | experimental | calculated | |
| Humic acid (HA) | 0 | 4 | — | — | 0.06 |
| *n*-Decylammonium humate (DAmH) | 50.8 | 3.200 | 27.61 | 27.59 | 0.42 |
| *n*-Dodecylammonium humate (DDAmH) | 54.8 | 2.800 | 31.55 | 31.67 | 0.53 |
| *n*-Tetradecylammonium humate (TDAmH) | 58.3 | 2.485 | 35.55 | 35.74 | 0.88 |
| *n*-Hexadecylammonium humate (HDAmH) | 61.2 | 2.125 | 41.58 | 39.81 | 1 |
| *n*-Octadecylammonium humate (ODAmH) | 63.8 | 2.075 | 42.57 | 43.88 | 0.98 |

layers, determined as a function of the chain length. In the Brindley model the slope of the function $d_{001}=f(n_C)$ is a projected distance-increase related to the increase in chain length. Its value for an alkyl chain orientation perpendicular to the flakes, and taking into consideration the valence angle of 109°28′ between the carbon atoms, is 1.27 Å. At smaller inclination angles the values can only be smaller. However, if the experimental $\Delta d_{001}/\Delta n_C$ is higher than above, the alkylammonium cations form a double layer in the space between the flakes. The slope of the line in Fig. 2 is 2.035 Å, so a double layer is formed, *i.e.* the increase in the two alkyl chains occurs additively. The inclination angle of the humate flakes and the alkyl chains ($\varphi$) can be calculated from simple geometrical reasoning. $d_{001}$ is the perpendicular distance between the flakes. The perpendicular projected length of two C—C distances is 2.54 Å. The experimentally determined 2.035 Å is also two

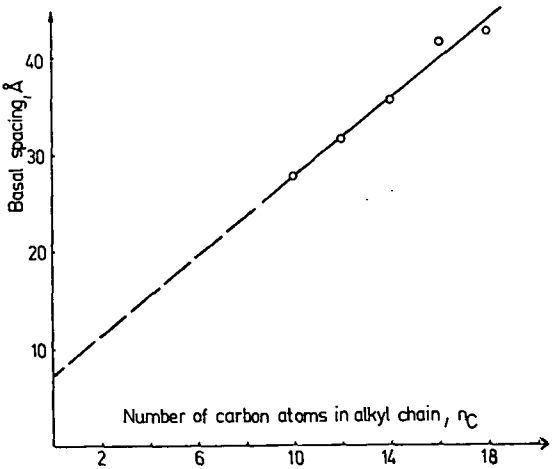


*Fig. 2.* Variation in basal spacing with length of alkyl chain in primary alkylammonium humates

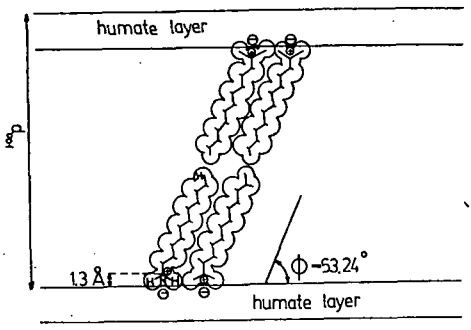


*Fig. 3.* Scheme of intercalated alkylammonium humate complex

C—C distances, *viz.* a perpendicular projection of the projected C—C distance of 2.54 Å for a given alkyl chain orientation (see Fig. 3). In the present case the angle of inclination of the alkyl chain and humate flakes is as follows:

$$\sin \varphi = \frac{\Delta d_{001}/\Delta n_C}{2.54} = \frac{2.035}{2.54},$$

$$i.e. \quad \varphi = 53.24°.$$

On the basis of the model, the most likely angle of inclination of the alkyl chains, taking into consideration the valence angles, is 55°. There is good agreement between the two values. With a similar method, the value for montmorillonite complexes was 65° [15].

With the $\lim_{n_C \to 0} d_{001}$ extrapolation, the thickness of the humate flakes can be calculated. Twice the distance between the imaginary plane of the humate flakes and the N atom of the ammonium cation (which the Brindley model gives as 1.3 Å) must be subtracted from the extrapolated value (7.25 Å). On this basis, the thickness of the humate flakes is 4.65 Å. The scheme based on the model can be seen in Fig. 3. The $d_{001}$ distances calculated in the case of alkyl chain orientation for the alkylammonium humate intercalation complexes in terms of the Brindley model are given in Table I. Comparison of the experimental and calculated values demonstrates very good agreement.

## *Conclusions*

The experimental results and the useful application of the Brindley model for lamellar-structure clay minerals seem to indicate clearly that the examined humic acid has a layer structure. If originally there had not been lamellae, but spheres or statistical coils in the humate solution, then the ion-exange of the alkylammonium cations would not have resulted in a change like this in the X-ray diffractograms. The reason why the diffraction pattern of the humic acid is so diffuse (see Fig. 1) is that there are not enough parallelly arranged lamellae in the powder samples to result in X-ray interference of satisfactory intensity. In the alkylammonium humates, however as a result of the van der Waals interaction between alkyl chains longer than 8 carbon atoms the lamellae become arranged in parallel. The fact that the X-ray reflections become more and more intense and sharp with increase of the alkyl chain length indicates the formation of more ordered structures.

The thickness of the humate layers can be calculated by extrapolation, but also from the experimental results which can be evaluated subsequently. The value 4.65 Å is realistic and corresponds to the structure conceived by HAWORTH [5] and SCHNITZER [3] (a polycondensed aromatic ring system bound by hydrogen-bonds).

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## РЕНТГЕНОГРАФИЧЕСКОЕ ИЗУЧЕНИЕ ИНТЕРКАЛЯЦИОННЫХ КОМПЛЕКСОВ АЛКИЛАММОННЫХ-ГУМАТОВ

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Заменили гуматные катионы эквивалентными количествами алкиламмониевых катионов с длиной цепи алкильного радикала $C_{10}$—$C_{18}$. Рентгенографическое исследование полученных образцов показало, что образующиеся структуры аналогичны минералам смектитного типа. Рассчитаны расстояния между слоями гуматов и определены углы наклона алкильных цепей к плоскостям структуры.